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BASELINE ACIDITY OF ANCIENT PRECIPITATION FROM THE
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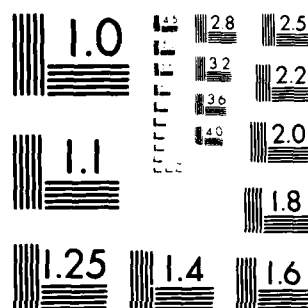
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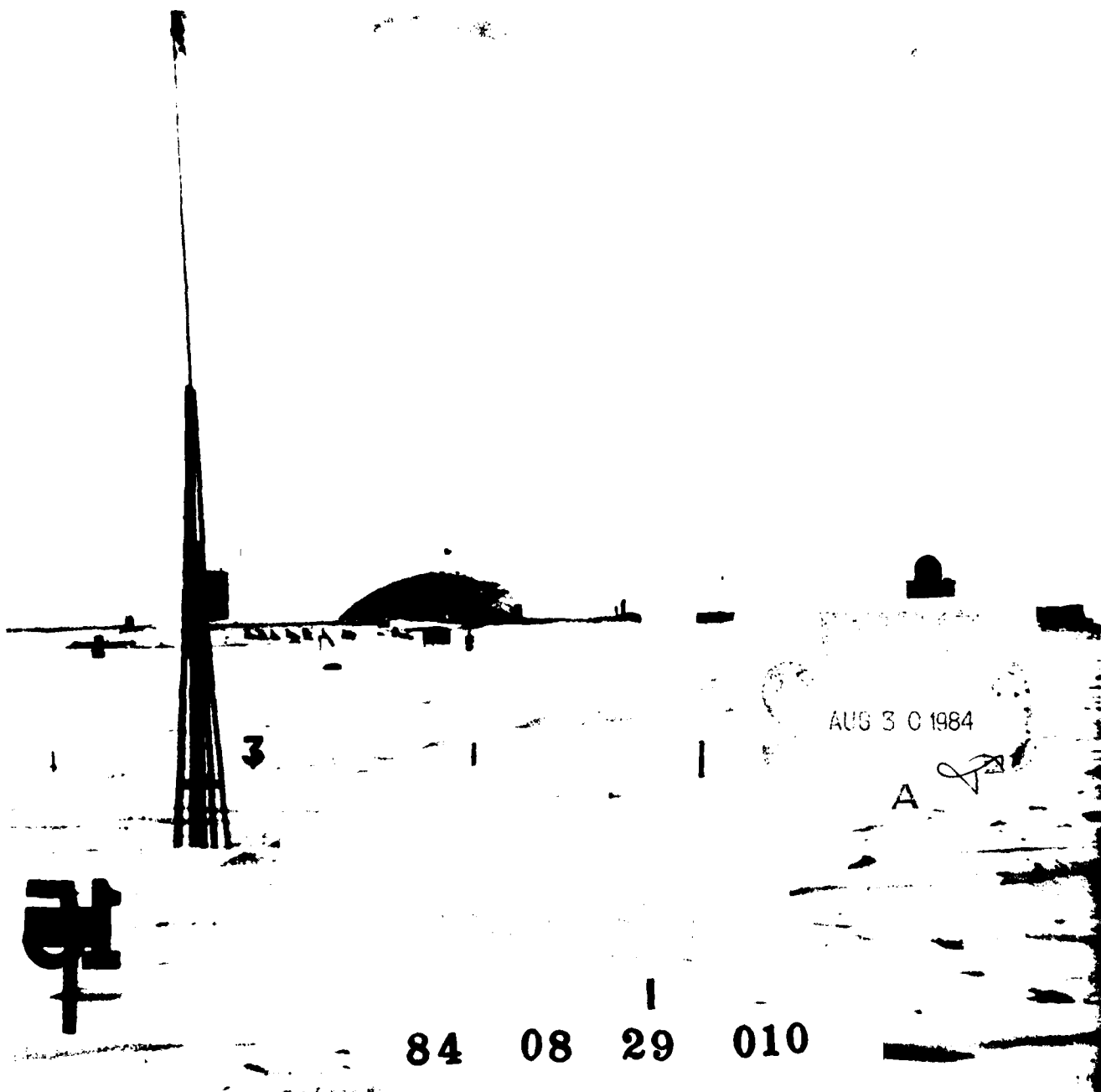


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Baseline acidity of ancient precipitation from the South Pole

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For conversion of SI metric units to U.S./British customary units of measurement consult ASTM Standard E380, Metric Practice Guide, published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

Cover: South Pole Station, January 1982. Location of geographic South Pole is marked by tripod-based tower in the left center foreground. Living facilities are contained in the geodesic dome (center) and the clean air facility is the dome-topped structure (right center).

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Baseline acidity of ancient precipitation from the South Pole

J.H. Cragin, M.B. Giovinetto and A.J. Gow



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PREFACE

This report was prepared by James H. Cragin, Research Chemist, Snow and Ice Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory; Dr. Mario B. Giovinetto, Chairman and Professor, Department of Geography, University of Calgary, Alberta, Canada; and Dr. Anthony J. Gow, Research Geologist, Snow and Ice Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory.

The National Science Foundation provided logistical support. The authors thank the Polar Ice Coring Office of the University of Nebraska and Dr. Gerald Holdsworth of Environment Canada for procuring the 200-m South Pole core. The authors also thank Eric Peake of the University of Calgary for preliminary analyses of SO_4^{2-} and NO_3^- , and Dr. Joseph L. Oliphant and Daniel C. Leggett of CRREL for reviewing the manuscript.

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BASELINE ACIDITY OF ANCIENT PRECIPITATION FROM THE SOUTH POLE

J.H. Cragin, M.B. Giovinetto and A.J. Gow

INTRODUCTION

Most studies of acid precipitation have used relatively recent rain or snow samples from either populated (Cogbill and Likens 1974, Galloway et al. 1976, Wolff et al. 1977, Brezonik et al. 1980, Lewis and Grant 1980) or remote (Weiss et al. 1977, Sequeira 1981, Galloway et al. 1982, Jickells et al. 1982, Koerner and Fisher 1982, Pszenny et al. 1982, Keene et al. 1983) locations. While remote precipitation is generally less acidic than that from industrialized areas, even samples from remote locations are often more acidic than the pH 5.65 expected from dissolution of atmospheric CO_2 . (See Appendix A for derivation of the effect of CO_2 on the acidity of pure, i.e., distilled, water.) A major concern is whether this excess acidity is of natural or anthropogenic origin. Acid rain on Bermuda has been ascribed to long-range atmospheric transport of sulfates and nitrates from North America (Jickells et al. 1982). Galloway et al. (1982) recently measured the pH of precipitation from five remote areas of the world and attributed much of the acidity at these locations to long-range transport. The well-known arctic haze over Alaska is believed to be caused by northward transport of pollutants from Eurasia and North America to the Arctic during winter (Rahn 1981). Because of potential long-range transport, the possibility always exists that present-day precipitation, however remote its location, will contain anthropogenic H_2SO_4 or HNO_3 .

One way to eliminate the anthropogenic component is to use samples of polar snow and ice that were deposited before the industrial revolution and are now preserved chronologically in permanent ice sheets. Impurities are incorporated into the snow by rainout, washout and dry fallout, and polar snow and ice samples have been used extensively to provide natural background concentrations and enrichments of many pollutants, especially metals (Cragin et al. 1975, Herron et al. 1977, Boutron and Lorius 1979, Weiss et al. 1979, Boutron 1980, Boutron 1982). The only pH measurements reported for pre-1800 liquid samples are those of Koerner and Fisher (1982), who found a mean Holocene (200-5500 years B.P.) pH of 5.48 in cores from the Agassiz Ice Cap, Ellsmere Island, Canada. However, no attempt was made to eliminate or control CO_2 -induced acidity which could introduce variability in the background pH results (Koerner and Fisher 1982). Titrations of acidity in ancient (30,000 years B.P.) ice core samples from Dome C, Antarctica ($74^\circ 39' \text{S}$, $124^\circ 10' \text{E}$) gave an average H^+ concentration of $2.44 \mu\text{Eq/L}$ (Delmas et al. 1980), which is equivalent to a pH of 5.61. In similar titrations of seven deeper (800 to 900 m) samples from the Dome C ice core, Delmas et al. (1980) obtained an average acidity of $1.07 \pm 0.52 \mu\text{Eq H}^+/\text{L}$, corresponding to a pH of 5.97. These older samples, though, correspond to Wisconsin age ice when the acid-neutralizing terrestrial dust input to ice sheets was considerably higher than during the last 10,000 years (Cragin et

Table 1. Values for pH and corresponding acidities for firn and ice core samples from the South Pole, Antarctica.

Sample depth (m)	Age in years before 1982 (est. error $\pm 5\%$)	N_2 atmosphere			Air	
		pH after 15 min.	pH after 30 min.	$[H^+]$ ($\mu Eq/L$)	pH	$[H^+]$ ($\mu Eq/L$)
7.72- 7.92	40	5.62	—	2.40	5.37	4.27
14.63- 14.82	90	5.61	—	2.45	5.34	4.57
20.00- 20.15	130	5.57	—	2.69	5.42	3.80
39.72- 39.84	270	5.72	—	1.91	5.37	4.27
59.00- 59.13	440	5.73	—	1.86	5.48	3.31
79.05- 79.15	640	5.69	—	2.04	5.42	3.80
101.26-101.39	860	5.51	—	3.09	5.33	4.68
120.54-120.65	1070	5.68	—	2.09	5.38	4.17
141.00-141.15	1300	5.83	5.79	1.62	5.40	3.98
160.00-160.12	1530	5.90	—	1.26	5.38	4.17
179.12-179.27	1750	5.47	—	3.39	5.24	5.75
200.39-200.53	2000	5.64	5.62	2.40	5.32	4.79
Average and standard deviation*		5.64 ± 0.08		2.27 ± 0.60	5.37 ± 0.08	4.30 ± 0.62

*Standard deviations shown mainly represent variability between sample concentrations rather than analytical precision.

al. 1977, Briat et al. 1982). Here we present values of pH from both air-saturated and CO_2 -free South Pole ice core samples spanning the last 2000 years (Table 1).

EXPERIMENTAL METHODS

A 200-m-long, 10-cm-diameter ice core was recovered from the Amundsen-Scott South Pole Station (Fig. 1) during the 1981-82 austral summer using an electromechanical drill (Rand 1976, Kuivinen et al. 1982). The core was dated stratigraphically (Fig. 2) along its entire length (Kuivinen et al. 1982, Gow et al., in prep.) by continuous counting of coarse-grained depth hoar layers that are known to occur on an annually repeating basis (Giovinetto 1960, Gow 1965). With this technique, age errors increase with depth because of missed years ascribable to hiatuses in accumulation. However, the error is estimated not to exceed 100 years for the deepest and oldest (approximately 2000 years B.P.) portion of the core.

The core was transported frozen to the U.S. for subsequent analysis at CRREL. For the chemical measurements reported here, we used 10- to 20-cm-long half-core segments, each representing exactly one year's accumulation to eliminate chemical variability due to seasonal concentration differences (Langway et al. 1975). The first three samples from depths of 7.72-7.92 m, 14.63-14.82

m and 20.00-20.15 m are of snow deposited since the onset of the industrial revolution. Older samples were selected at 20-m intervals.

All subsequent laboratory work including sample cleaning, melting, deaeration and analysis was performed in a Class 100 clean room. Utensils and labware (Teflon, polyethylene) used to clean the core or contain sample meltwater were cleaned by rinsing first with distilled-deionized water, then by rinsing with electronic grade acetone and finally by leaching for 3 days with 18 megohm Milli-Q deionized water. Surface contaminants were removed from sections of firn core samples* by mechanically scraping off the outer 1.0 cm with a stainless steel chisel. This process was conducted within a Class 100 laminar-flow clean air station in a coldroom using extreme care to allow cleaned areas of the core to contact only cleaned Teflon (FEP) or polyethylene (LPE). Deeper core samples (depth range 120-200 m) consisting of imper-

*On polar ice sheets snow is transformed into ice by compaction of the permeable firn which composes the upper 115 m at the South Pole. However, there is no evidence to indicate any significant change in the acidity of the snow caused by post-depositional diffusion of air through the permeable firn. Observations in support of this include the very sharp nature of changes in the chemical composition (Boutron 1982) of firn from the South Pole and Dome C, Antarctica. Broader peaks would have been expected if post-depositional diffusion of air through the firn was contributing significantly to the measured chemical concentrations.



Figure 1. Core drilling site, located approximately 800 m from South Pole Station geodesic dome. The drill tower and electromechanical drill can be seen emerging from the roof of the wind-shelter tent. Scientist in foreground is carrying the inner drill barrel from which an ice core, approximately 1-m long, will be extracted.



Figure 2. Scientist logging a core section for length and stratigraphic features.

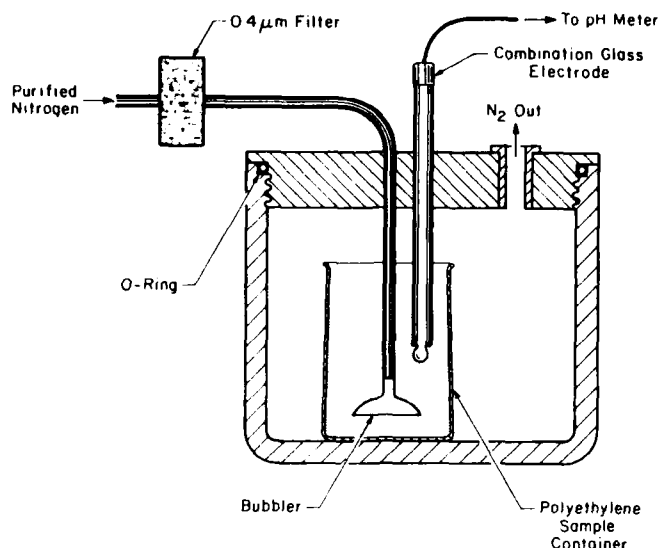


Figure 3. Schematic of apparatus used for CO_2 -free pH measurements.

meable glacial ice were cleaned in a Class 100 clean room by repeated washings with 18 megohm Milli-Q deionized water as described elsewhere (Langway et al. 1974, Cragin et al. 1975, Herron et al. 1977). Immediately after cleaning, these samples of firn or ice were placed in individual wide-mouth polyethylene (LPE) bottles and allowed to melt. After each melted sample had reached room temperature ($25 \pm 1^\circ\text{C}$), it was deaerated by bubbling filtered ($0.4 \mu\text{m}$) purified nitrogen gas through it for 15 minutes to remove CO_2 and eliminate pH variability caused by differing amounts of H_2CO_3 . Additional deaeration (Table 1, fourth column) produced no significant pH change, indicating that 15 minutes was sufficient. The sample pH was then measured under a nitrogen atmosphere in a specially constructed plexiglass chamber (Fig. 3). Samples were then allowed to equilibrate overnight in the dark with air and measurements were again made to determine the pH of CO_2 -saturated samples.

All pH measurements were made with an Orion model 81-03 combination Ross electrode. This electrode differs from ordinary combination pH electrodes in that the reference half cell potential is controlled by reversible redox equilibria rather than by the conventional calomel or Ag/AgCl . Compared to a conventional combination pH electrode, the Ross electrode responded more rapidly and showed negligible drift even in low ionic strength solutions of South Pole meltwater.

The precision and accuracy of these measurements is estimated to be ± 0.05 pH unit.

RESULTS AND DISCUSSION

The values for pH and corresponding calculated acidities presented in Table 1 are for 12 annual increments of South Pole core covering approximately the last two millennia. Important features of these data include the uniformity of pH values and the absence of any appreciable trend in pH over the core profile. The lack of an observed increase in acidity (decrease in pH) is probably due to the age of the samples; the most recent sample fell as snow 40 years ago, before "tall stacks" of the 1950s exacerbated the SO_2 transport problem.* Furthermore, since acid pollutants are generated mainly in the Northern Hemisphere, they may not reach the Antarctic Ice Sheet in measurable amounts because of poor interhemispheric mixing and because of washout and dry deposition during extended transport to Antarctica. This is supported by the absence of an increase of sulfate

*Snow layers younger than 1940 (above 7.7 m) were not sampled because of possible local contamination from South Pole Station, constructed and occupied since 1957. Future studies of pH in more recently deposited snow layers will include measurements on pit samples collected 10 to 20 km upwind of South Pole Station.

ion, a major component of acid precipitation, in cores covering the last 100 years from Dome C, Antarctica (Delmas et al. 1980, Delmas and Burton 1980). Our pH values thus provide a baseline or reference pH against which present-day precipitation can be compared.

Another important aspect of the data is the actual magnitude of the pH values themselves. For the air-equilibrated samples, the average pH is 5.37 ± 0.08 —about twice as acidic as the 5.65 pH expected for “pure” rainwater in equilibrium with atmospheric CO_2 . The average pH of deaerated samples is 5.64 ± 0.08 . The difference of 0.27 pH units between aerated and deaerated samples is about what would be expected from dissolution of atmospheric CO_2 ; air-saturated water contains 2.2×10^{-6} Eq H^+/L from H_2CO_3 dissociation, which would lower a 5.65 pH sample by 0.28 pH units. Converting the above aerated and deaerated pH values to H^+ concentrations (Table 1, fifth and seventh columns) shows that half of the acidity is caused by CO_2 dissolution and half by other naturally occurring acids. Preliminary ion chromatographic measurements of SO_4^{2-} and NO_3^- concentrations in eight samples gave concentrations of 1.0 – 2.1 $\mu\text{Eq SO}_4^{2-}/\text{L}$ and 1.5 – 2.2 $\mu\text{Eq NO}_3^-/\text{L}$. Based on Na^+ concentrations (0.57 – 1.4 $\mu\text{Eq}/\text{L}$) measured in four samples, the sea salt contribution to SO_4^{2-} is calculated not to exceed 10% of the total SO_4^{2-} present in the samples. The average sum of SO_4^{2-} and NO_3^- concentrations, 3.3 $\mu\text{Eq}/\text{L}$, is more than enough to balance the average 2.3 $\mu\text{Eq}/\text{L}$ of H^+ (pH 5.64) in the deaerated samples. Thus, on a molar equivalent basis the pH of deaerated samples can easily be accounted for by the SO_4^{2-} and NO_3^- concentrations if these ions originate from H_2SO_4 and HNO_3 . Some acidity may also be contributed by weak organic acids (acetic, formic), but we have no experimental evidence to support this.

Electrolytic conductivities of the deaerated samples ranged from 1.0 to 1.7 $\mu\text{mho}/\text{cm}$ and correlated well ($r = 0.87$, $p = 0.01$ for 6 d.f.) with values calculated from the observed pH's and ion concentrations. Most of the background H_2SO_4 present in the ancient precipitation samples reaches the South Pole through advection as well as subsidence from the upper troposphere and lower stratosphere, which facilitate direct contribution from the “Junge layer,” a good source of H^+ that is replenished by violent and nonviolent volcanic eruptions (Berresheim and Jaeschke 1983).

Alkaline minerals contained in airborne particulate matter can neutralize acidity in precipitation, resulting in lower background acidity (higher pH).

Greater dust content may be the reason for higher pH values found in ancient ice samples from Baffin Island by Koerner and Fisher (1982). But the concentration of terrestrial dust at the South Pole is very low (less than 0.25 $\mu\text{Eq Ca} + \text{Mg}$) (Boutron 1982) and most of the Ca and Mg present probably originates from sea salt rather than from acid-neutralizing minerals. Thus, the acidity of South Pole samples is a good representation of background levels without undue influence from wind-transported dust. Samples from less remote locations on the globe, with local or regional dust sources, would be expected to have higher pH values for similar acid inputs.

CONCLUSION

Our results, showing South Pole ice deposits to be a factor of two or more acidic than the presumed pH of 5.65 , confirm the postulation of Charlson and Rodhe (1982) that the natural acidity of pristine precipitation is indeed greater than that expected from H_2CO_3 equilibrium alone. Thus, in assessing anthropogenic contributions to present-day precipitation, a pH of 5.4 is probably more representative of natural background conditions than the generally accepted value of 5.65 .

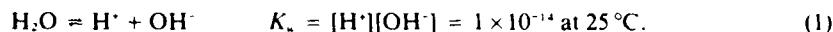
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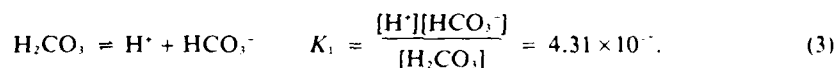
APPENDIX A: EFFECT OF CO₂ ON ACIDITY OF PURE WATER

Water is a very weak electrolyte and undergoes self-ionization to produce hydrogen and hydroxyl ions according to the equation

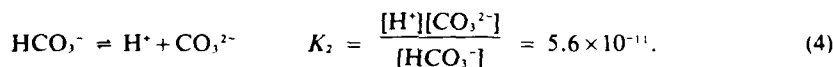


Mass balance considerations indicate that ionization produces equal numbers of H⁺ and OH⁻ ions, and thus pure water is neither acidic nor basic. At 25°C, only 0.00000018% of the water molecules are ionized, resulting in [H⁺] = [OH⁻] = 1 × 10⁻⁷ mol/L, which is equivalent to a pH of 7.00. The degree of ionization increases with temperature so that a neutral solution has a pH of 6.5 ([H⁺] = 3.16 × 10⁻⁷ mol/L) at 100°C and a pH of 7.4 ([H⁺] = 3.98 × 10⁻⁸ mol/L) at 0°C. Our concern here is with solutions at 25°C and subsequent discussion will be restricted to this temperature.

In actual practice, however, pure water in contact with atmospheric air does not have a pH of 7 because of dissolution of CO₂, an acidic gas. Carbon dioxide forms carbonic acid, which dissociates to form hydrogen and bicarbonate ions. The equilibria can be shown as



Subsequently, bicarbonate ion can dissociate to produce carbonate and additional hydrogen ions:



The first equilibrium constant K_1 shows that only about 6% ($\sqrt{4.31 \times 10^{-7}}$) of the H₂CO₃ (actually CO₂ + H₂O) dissociates to form H⁺ and HCO₃⁻ ions. The second equilibrium constant K_2 shows that of the 6% HCO₃⁻, only about 0.00075% ($\sqrt{5.6 \times 10^{-11}}$), dissociates to form CO₃²⁻ and additional H⁺ ions in neutral solution. However, the solution is not neutral because of H⁺ ions from the first dissociation; the presence of these ions suppresses the second ionization (H⁺ drives the equilibrium in eq 4 to the left). The net result is that the contribution of H⁺ from the second dissociation is very small and can be neglected.

Using the first dissociation, eq 3, we can calculate the H⁺ concentration and hence pH of a solution of known CO₂ content. Air-saturated water contains 1.35 × 10⁻³ mol/L CO₂ at 25°C (Kolthoff et al. 1969). Thus, if we let $x = [\text{H}^+] = [\text{HCO}_3^-]$ then $[\text{H}_2\text{CO}_3] \approx (1.35 \times 10^{-3}) - x$. Substituting into eq 3

$$\frac{x^2}{(1.35 \times 10^{-3}) - x} = K_1 = 4.31 \times 10^{-7}$$

and the quadratic solution yields

$$[\text{H}^+] = 2.2 \times 10^{-6} \text{ mol/L}$$

which corresponds to a pH of 5.65.

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